

Technetium Management Program Plan - 17376

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ABSTRACT

Technetium management is a high-priority activity for the U.S. Department of Energy (DOE) Office of Environmental Management (EM) complex. Waste management and remediation issues involving technetium represent environmental risks and challenges that are unique to DOE. This plan lays out the technology development activities that are underway as well as future technology needs to address technetium issues across DOE EM sites and across programmatic areas of tank waste, groundwater and soils, and facility decommissioning and deactivation in order to be comprehensive and to allow integration of similar activities. The program was developed in close coordination with site representatives and program offices.

Activities and needs that were identified share common themes and were grouped into areas of characterization, treatment, and disposition. Characterization includes understanding the inventory at particular locations, the chemical species, and chemical and physical behavior, whether in a treatment process flowsheet or a geological setting that displays periodic contaminant releases. The tools for characterization in these different environments might use the same sensors or protocols. Treatment options include methods to capture technetium such as ion-exchange or manipulation of oxidation states, which also may be applied across program areas. Disposition includes end-points of the processes and environmental risk, including waste form behavior, mobility of technetium once it is treated or remediated, and long-term monitoring. Disposition represents integration of all cleanup actions at a site.

INTRODUCTION

Among radioactive constituents present in tank waste and as a contaminant in the environment, technetium-99 (⁹⁹Tc) presents a unique challenge because of its radiotoxicity, long half-life (213,000 years [1]) and complex chemical behavior [2,3]. Technetium is generally mobile in the subsurface, but non-mobile species also appear to be present. The vast majority of ⁹⁹Tc inventory is present in tank wastes, but its presence in vadose zone and groundwater plumes drives risk and affects remedial decision-making at multiple U.S. Department of Energy (DOE) sites. Technetium is a byproduct of nuclear weapons production activities, a man-made element only found in nature under rare circumstances. The predominant

perchnetate species is volatile at temperatures that would be used in vitrification treatment, which makes incorporation of Tc into a vitrified waste form a challenge for nuclear waste management. There are no isotopes of technetium that are non-radioactive, which caveats any experimentation with simulants. Thus, the issue of technetium management presents problems specific to DOE that would not likely be encountered or resolved outside the Department, and therefore represents a priority area for technology development by DOE.

Table 1 summarizes the inventory and disposition of ⁹⁹Tc at sites within the DOE EM complex. The primary sites include the DOE EM Richland Operations Office (RL) and the Office of River Protection (ORP) at the Hanford Site, the Savannah River Site (SRS), and the Paducah Site known as the Paducah Gaseous Diffusion Plant (PGDP).

DOE-EM has a critical need to resolve scientific and technical issues underpinning the ability to safely, cost-effectively, and efficiently

- process and immobilize tank waste,
- remediate contaminated vadose zone and groundwater plumes, and
- decontaminate and decommission facilities.

The current approach to addressing these technical issues relies in part on assumptions (chemical behavior, mobility, disposition within a flow sheet). Those assumptions contain uncertainties that result in conservative actions or overdesign of facilities. To reduce technical uncertainties associated with the long-term environmental impact of ⁹⁹Tc, an integrated program is needed to evaluate options for treatment and disposition of ⁹⁹Tc present in the tank waste, groundwater, and soil.

Table I. Estimated Technetium Quantity in the DOE-EM Complex^a

Site	Amount (Ci)	Location/Disposition
Hanford ^b	26,500	Tanks (eventual disposal on-site or repository)
	700	Leaks and direct discharges released to sediment (groundwater & vadose zone)
	50	Burial grounds (non-DOE)
Savannah River ^c	41,500	Tanks
	980	Saltstone
	400	Glass canisters
Paducah ^d	255	Contaminated equipment (cascades), eventual disposal on-site
	126	Nickel ingots
	3825	Groundwater and soil contamination
Portsmouth	94	Contaminated equipment (cascades), eventual disposal on-site
Idaho	3450	Calcine

	224	Sodium bearing waste
West Valley	1700	Immobilized as high-level waste glass and low-level waste cement

^a Tc for cleanup disposition, not including spent fuel

^b 32,600 Ci produced at Hanford (1922 kg), 7000 Ci shipped off-site with uranium. Estimated Tc in groundwater and vadose zone taken from Serne et al. [5], but other estimates are as high as 1000 Ci.

^c SRS estimates and characterization through Sept 2014

^d 11400 Ci (670 kg) shipped to Paducah, most shipped out with enriched uranium. Recent (2011-2014) sampling indicates 85-425 curies of remain in cascades. Samples of the nickel ingots from 2007 indicate an estimate in the range of 17-225 curies with 126 as the average. A rough order of magnitude estimate for the soil and groundwater based on plume area and other factors yields a range of 1913 to 5738 curies.

SCOPE

A Tc management program is proposed that addresses the entirety of environmental remediation and the waste treatment flowsheet from source terms (i.e., waste tanks, facilities, and environmental disposal structures such as cribs, trenches, and ponds) through waste processing and immobilization, to disposition and long-term management. This plan encompasses the technical activities designed to reduce uncertainties, validate assumptions, and explore technical alternatives that are critical for the management of ⁹⁹Tc. This planning will enable

- establishment of key performance measures in cleanup where they are absent;
- development of treatment options that reduce life-cycle cost and better address environmental risk;
- establishment of priority activities based on specific goals and success criteria;
- development of detailed work plans focused on these goals and performance measures;
- meaningful interactions between DOE site offices and contractors, regulators, and stakeholders; and
- development of realistic long-range plans that encompass strategic direction, project activities, regulatory milestones, and key decision points.

The Tc management program will integrate and advance current understanding of source terms, chemistry, separations, subsurface environmental behavior, and waste form performance. The program will provide viable technical solutions, applicable across all DOE sites, with clear baseline insertion points and options for long-term management. The technical roadmap presented in this document identifies ongoing activities, as well as additional knowledge gaps that will guide experimental studies and programmatic activities designed to reduce uncertainties or to validate assumptions that are critical for the management of ⁹⁹Tc.

TECHNICAL ROADMAP

The technical roadmap includes ongoing and future technology development funded by DOE EM Headquarters (HQ) (Waste Processing, Soil and Groundwater Remediation, and Deactivation Decommissioning), as well as DOE site offices and contractors. Technical needs for the roadmap were developed as part of planning. The primary methods of identifying these needs were to solicit input from DOE EM site offices and contractors, coordinated with technical input from the national laboratories (PNNL and SRNL). These needs will be addressed through collaboration between DOE field sites, site contractors, and Headquarters. The technical needs were categorized into three major program elements: (1) characterization (inventory of source terms, measurement, speciation, and chemistry); (2) treatment options (immobilization and remediation); and (3) disposition (behavior in the environment, risk-based remediation endpoints, and monitoring).

There is considerable overlap of needs identified at the different sites. As an example, a number of complex technical issues with ^{99}Tc management were identified for the Hanford Site, providing opportunities for insertion of options to reduce current uncertainties and mitigate technical risks posed by ^{99}Tc related to completing the Hanford Site cleanup mission.^a However, the survey of needs demonstrated that solutions for technical challenges faced by the Hanford Site are extensible to comparable challenges at the other DOE EM sites, including SRS and Portsmouth and Paducah.

The characterization program element will develop the analytical tools necessary to enable improved detection and quantification of ^{99}Tc species; resolve the scientific uncertainties underpinning ^{99}Tc chemistry and speciation; identify the processes by which ^{99}Tc behaves in tank waste and interacts with subsurface geologic media; and establish the basis to quantify environmental risks and define appropriate remediation actions and goals. Characterization is critical because the chemical form of ^{99}Tc dramatically influences its behavior. The most common oxidation state is +7, which is normally pertechnetate ion (TcO_4^-) and is highly soluble. Reduction to the +4 state typically causes it to form technetium oxide (TcO_2), which is insoluble. Other oxidation states, such as +1, are also possible, and the soluble “non-pertechnetate” in tank waste is believed to be in the +1 state [4]. The stability, kinetics of transition, ability to analyze, and fate and transport of ^{99}Tc are highly dependent on the redox state and the nature and stability of the form of lower oxidation state species is not well understood at this time. The synthesis of potential compounds involves moderately complex synthesis routes and yield products with varying degrees of stability. It is fundamentally important to have the ability to identify and quantify ^{99}Tc species in order to manage its treatment and disposition.

The treatment and remediation program element is focused on improving ^{99}Tc retention and immobilization, quantifying waste form performance, providing

^a Swanberg, DA, *Washington River Protection Solutions, personal communication regarding the strategy for management and disposition of ^{99}Tc in Hanford tank waste.*

rationale for establishing appropriate remediation targets that incorporate relevant risk factors, and developing remediation approaches, such as monitored natural attenuation (MNA) and enhanced attenuation, that reduce contaminant migration and reduce risk to human health and the environment. For ^{99}Tc in soil and groundwater plumes, the treatment and remediation program element is based on characterization of controlling processes and mass flux. For waste processing, the program element includes combining immobilization with treatment methods to meet risk goals and developing separation processes that are integrated with speciation and inventory characterization tasks.

The disposition program element is focused on providing the technical basis for risk-informed remediation endpoints and performance assessments using results from the characterization and treatment/remediation program elements. The disposition program element will engage scientific and engineering experts to provide options and capabilities for use and synergy across waste processing and soil and groundwater activities. This program element will develop options for disposal and remediation that meet performance goals and will help define risk-based treatment and remediation end points to ensure appropriate disposition paths are selected.

The task activities, scope and outcomes, schedule, and logic for task activities are described in Table 2. Figure 1 illustrates the elements and timelines.

There are no current plans for separation of ^{99}Tc from the tank waste nor for disposition. As such, the activities outlined in the plan associated with tank waste treatment of ^{99}Tc do not directly influence baseline scheduled activities. However, there are a number of insertion points for new technologies associated with ^{99}Tc separation and disposition for Hanford tank waste. The first insertion point is associated with tank farm processing for direct feed low-activity waste [LAW] to vitrification. The next opportunity is associated with the Effluent Management Facility Bottoms Direct Disposal and processing of off-gas condensate. The final opportunity is associated with supplemental or alternative LAW immobilization and disposition

Table II. Technetium Management Plan Task Descriptions

Program Element	Focus Area	Activity	Task (Sponsor)	Outcome and Scope
Characterization	Speciation and Chemistry	Redox Chemistry	^{99}Tc redox speciation in low-activity waste (LAW) (HQ) (3)	Provide a technical basis for developing treatment methods for ^{99}Tc in waste streams. To develop technically viable and practical options for treatment and/or removal of total ^{99}Tc from the Hanford tank waste streams, the composition, chemical properties (redox

Program Element	Focus Area	Activity	Task (Sponsor)	Outcome and Scope
				state and adsorption properties), and stability of non-pertechnetate species need to be characterized and quantified.
		Thermodynamics and Kinetics	Quantify effect of co-mingled contaminants on ⁹⁹ Tc behavior, transport, and fate (RL)	Identify biogeochemical processes affecting ⁹⁹ Tc behavior in co-mingled contaminant plumes. Groundwater contamination often includes a complex mixture of metals, radionuclides, cations, and organic solvents, which may impact in situ treatment methods. Laboratory experiments and predictive simulation will be used to examine the impacts of amendments on redox, adsorption properties, and species stability. Reactive transport models will be developed to understand the interaction between contaminants.
			Define and quantify variables affecting biogeochemical controls on ⁹⁹ Tc behavior in soil and groundwater plumes (RL)	Evaluate and implement natural attenuation of ⁹⁹ Tc in the subsurface by biotic and abiotic processes. The technical understanding of biogeochemical controls on ⁹⁹ Tc fate and transport in the subsurface needs to be developed as well as generating relevant thermodynamic data on adsorption and solubility for ⁹⁹ Tc in the subsurface.
	Measurement Techniques	Non-Pertechnetate	Develop methods to quantify ⁹⁹ Tc compounds in tank waste	Develop an analytical test method usable in 222-S lab to determine the fractional amounts of ⁹⁹ Tc, both pertechnetate, and non-

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			(Washington River Protection Solutions [WRPS]) (3, completed)	pertechnetate in Hanford tank waste that can be implemented to establish a data set of ⁹⁹ Tc species in the Hanford tank waste. This data set will be used in future processing of waste where immobilization and/or removal of ⁹⁹ Tc is a significant step.
			Quantification and Identification of non-pertechnetate in tank waste samples (HQ) (3)	Characterize ⁹⁹ Tc speciation in the Hanford tank waste to support waste demonstrations. Samples of actual Hanford tank supernatants and saltcakes that contain ⁹⁹ Tc species, particularly non-pertechnetate, are needed to perform characterization and testing. This effort will identify the most relevant waste samples and arrange their shipping from the Hanford 222-S facility to PNNL's 325 Building. The tank waste samples will be processed to reduce radiation dose by removing ¹³⁷ Cs and analyzed for ⁹⁹ Tc speciation. This effort supports other tasks focused on developing processing options for non-pertechnetate species.
			Non-pertechnetate sensor development (HQ)	Develop sensor to provide real time analysis of the concentration of non-pertechnetate species in tank waste. This sensor will enable real-time measurement of non-pertechnetate in tank waste, allowing for new processing approaches, and will eliminate the need for extensive laboratory testing to quantify the amount of non-pertechnetate present in tank waste. The most recent focus

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				has been on ⁹⁹ Tc(+1) carbonyl compounds.
		In Situ/Real-Time Process Measurement	Real-time/in situ characterization and monitoring for geochemical and microbial properties and reactions (New)	Implement monitoring approaches that are more cost-effective than those currently used in point-based measurements at wells. Develop real-time/in situ characterization and monitoring approaches and tools that distinguish between species with different spectroscopic footprints (UV, IR, NMR, etc.) to quantify geochemical and microbial properties and reactions controlling natural attenuation and long-term remedial performance (sorption, redox, precipitation, etc.).
Source-Term Inventory		Facilities	Characterize ⁹⁹ Tc in cascades (New)	Characterize ⁹⁹ Tc leachability in the waste stream to determine if it exceeds limits for direct disposal, or if a remediation method needs to be implemented. This effort will provide the technical basis for disposal or remediation.
		Waste Streams	Quantify inventory and behavior of ⁹⁹ Tc in solid secondary waste streams and residuals – in particular high-efficiency particulate air filters and submerged bed scrubber/wet	Determine if ⁹⁹ Tc inventory and leachability in this waste stream exceed limits for direct disposal in the Integrated Disposal Facility (IDF), or if a remediation method needs to be implemented. This work will use methods to measure and calculate diffusion (or other mechanism) to determine leachability and help to define the amount of processing that must be performed to clean up ancillary

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			electrostatic precipitator equipment (New) (3)	equipment that is to be disposed of from the Waste Treatment and Immobilization Plant (WTP).
		Ground-water and Soil	Quantify waste sources for subsurface contaminants through chemical fingerprinting and data mining (New)	Provide a technical basis for developing remediation approaches, once waste sources are determined. Waste sources can be identified and quantified through chemical/spectroscopic fingerprinting and data mining of historical records. Speciation of contaminants in vadose zone and groundwater plumes can be compared with experimental results used to identify waste sources.
Treatment	Immobilization	Separation	⁹⁹ Tc removal from LAW recycle with Kurion media (WRPS) (2, completed)	Perform testing to develop a process to remove ⁹⁹ Tc from the off-gas recycle stream using Kurion media so that the decontaminated stream can be diverted to another pathway. The ⁹⁹ Tc could then be immobilized separately. This will divert substantial chloride, fluoride, and sulfate away from the WTP, substantially decreasing the quantity of immobilized low-activity waste (ILAW) produced over the mission life. Current scope involves removal of ⁹⁹ Tc and other contaminants by sorption and ion exchange.
			Maturation of Tc ion exchange (Superlig® 639) (WRPS) (3)	Complete maturation for SuperLig® 639 for removal of pertechnetate from LAW for current process conditions. Primary goal is for application to Supplemental LAW to develop an option to remove

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				<p>⁹⁹Tc and immobilize it in a low temperature waste form. Current scope examines ~1-L ion exchange columns processing a simulant of the high-density salt solution effluent expected from WTP Pretreatment Facility during Supplemental LAW operation.</p>
			<p>Evaluation of non-ion exchange methods for ⁹⁹Tc removal (New) (3)</p>	<p>Provide alternatives to the baseline that target the pertechnetate form. The options for removal of pertechnetate by non-ion exchange methods from LAW will be evaluated. The feasibility of non-pertechnetate oxidation to ⁹⁹Tc(+7) and separation as pertechnetate will be tested. The outcome of this effort will provide an alternative for removal of various forms of ⁹⁹Tc from LAW.</p>
			<p>Treatment and removal of non-pertechnetate species from LAW (HQ) (3)</p>	<p>Develop a method to remove total ⁹⁹Tc (pertechnetate and non-pertechnatate) from LAW. This will enable disposition of LAW in alternative waste forms. The current baseline involves disposition of ⁹⁹Tc in a glass waste form. Develop methods to study complexation and stabilization of pertechnetate species to drive materials design for treatment/removal.</p>
			<p>⁹⁹Tc removal from LAW off-gas recycle stream (HQ) (2)</p>	<p>Develop a process to remove ⁹⁹Tc from the off-gas stream so to create disposition options for the decontaminated stream and the technetium stream. This would divert substantial chloride, fluoride, and sulfate away from</p>

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				WTP instead of recycling to the LAW melter, substantially decreasing the quantity of ILAW produced over the mission life. Current scope involves optimizing parameters for precipitation as ⁹⁹ Tc(IV) oxide and removing it by filtration.
			Evaluate long-term operational stability of resins during use in ⁹⁹ Tc removal from aqueous streams (New)	Identify materials that can be used to treat groundwater contaminated with ⁹⁹ Tc over the long-term. A testing program has evaluated various commercial and engineered materials at the bench-scale for removal of contaminants of concern from Hanford groundwater, but long-term operational stability needs to be evaluated and compared with experimental data.
		Waste Forms	Understand, control, and improve ⁹⁹ Tc retention in glass processing (LAW and high-level waste [HLW]) (ORP)	Develop methods to improve ⁹⁹ Tc incorporation into LAW and HLW glass. Current approaches provide limited incorporation of ⁹⁹ Tc in LAW glass due to entrainment in the off-gas streams. This work will result in increased ⁹⁹ Tc glass loading. While pertechnetate is the predominant tank waste species, this task also explores volatility, redox, and other behavior of ⁹⁹ Tc(+1) carbonyl compounds in the melter environment.
			Flowsheet modeling improvements for LAW condensate recycle	Develop improved parameters and a technical basis for predicting the distribution of species from melters. Current approaches for WTP melters use simple "split factors" to

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			predictions (HQ) (2)	describe the fraction of individual components that partition to the off-gas as opposed to being retained in the glass. A better understanding of the off-gas composition is necessary to quantify recycle volumes and off-gas treatment options.
			Development of non-glass waste forms specifically for technetium immobilization (HQ) (2)	Develop non-glass waste forms for ⁹⁹ Tc using experiments and predictions to drive development of alternative materials. The goal is to provide a disposition path for ⁹⁹ Tc removed from either the LAW stream or the melter off-gas. This will allow diversion of these waste forms to alternative repository sites.
			Zirconium Metal Organic Frameworks for Pertecnetate Removal (HQ, International Program)	Develop novel class of thermal and aqueous stable metal organic frameworks (MOFs) for TcO ₄ ⁻ removal from liquid LAW. MOF materials are known to have superior adsorption properties, faster kinetics, and distribution coefficient (Kd) due to the high surface area (8000 m ² /g) and high density of chelating sites. This task is focused on developing MOF based materials for capture and immobilization of pertechnetate, providing a "game-changing" approach to address the issue of Hanford Waste Treatment and Immobilization Plant.
			Immobilization of Effluent Treatment Facility (ETF)	Develop a cementitious waste form using experiments and prediction that could be used to immobilize ⁹⁹ Tc in this waste

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			secondary waste (WRPS) (1)	stream. WTP operations will generate an evaporator condensate stream that will be treated at the ETF, but increased volume and changed composition of this stream are expected to exceed capacity of the ETF drier and may make a solid waste that does not meet Washington State Administrative Code disposal criteria.
			Measure properties of laboratory-prepared saltstone samples versus actual emplaced core samples and inline process samples (Savannah River Remediation [SRR])	Measure physical properties (e.g., hydraulic conductivity) of laboratory-prepared saltstone samples with actual emplaced saltstone core samples taken from SDU 2. This testing program will provide confidence that the laboratory- prepared simulated saltstone grout has similar properties to the emplaced saltstone grout and that modeling assumptions can be made on laboratory-prepared samples.
			⁹⁹ Tc leaching characteristics from Saltstone monolith (SRR)	Provide empirical leaching (diffusion) data for ⁹⁹ Tc and other saltstone contaminants that can be used as direct input to transport models and generate information regarding leaching with multiple pore volume exchanges. This task will establish the dynamic leaching behavior of saltstone contaminants.
		Encapsulation	Develop macroencapsulation technologies	Develop macroencapsulation technologies, such as specialized cementitious waste forms, to immobilize solid

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			for immobilization of solid secondary waste (New) (1)	secondary waste and sequester ⁹⁹ Tc. Use experiments and predictive simulation to study ⁹⁹ Tc encapsulation, resulting in technologies applicable to a range of solid secondary wastes, including cascades, ingots, off-gas equipment, hoses, and pumps.
		Sorption	Enhance adsorption or immobilization of ⁹⁹ Tc species in the subsurface to prevent plume migration (New)	Mitigate the flux of ⁹⁹ Tc from the vadose zone to groundwater and migration of groundwater plumes to uncontaminated regions of aquifers. Use experiments and predictive simulation to develop physical and biogeochemical methods for immobilization of ⁹⁹ Tc species in the subsurface using adsorption.
		Precipitation	Develop biogeochemical remediation approaches (HQ)	Provide technical guidance and support needed to implement remedial strategies for ⁹⁹ Tc in soil and groundwater. Biogeochemistry-based (combined chemical and biological) remedial strategies need to be developed for long-term immobilization of ⁹⁹ Tc in the subsurface (soil and groundwater). This includes post-remediation when the aquifer returns to normal/oxic conditions. The understanding for predicting and optimizing the long-term performance of these remedial strategies needs to be completed.
			Develop methods to alter ⁹⁹ Tc biogeochemical	Provide new in situ treatment methods for immobilizing ⁹⁹ Tc and co-contaminants using laboratory experiments, predictive simulation, and field

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			behavior in the presence of co-contaminants (RL)	investigations to evaluate the effects of amendments for biogeochemical treatment of contaminant mixtures. The use of combined remediation or treatment trains will be evaluated.
			Develop methods for use of reducing gases for in-situ remediation to immobilize ⁹⁹ Tc in subsurface (RL)	Reduce the flux of ⁹⁹ Tc from the vadose zone to groundwater. The technical foundation and primary scale-up data for gas-phase treatment of ⁹⁹ Tc in the vadose zone needs to be developed. Laboratory experiments have been performed demonstrating a robust treatment approach; scale-up data and simulations are needed.
Remediation		In Situ Subsurface Attenuation	Develop technically defensible basis for monitored natural attenuation for ⁹⁹ Tc in the subsurface (RL)	Provide a framework for evaluating MNA that can be applied to ⁹⁹ Tc in the vadose zone and groundwater. Technical data are needed to support MNA evaluation for ⁹⁹ Tc, consistent with existing guidance. The data will include information on vadose zone flux, waste chemistry, and conceptual models for ⁹⁹ Tc.
		In Situ Subsurface Attenuation	Improve risk reduction by enhanced attenuation methods (New)	Provide the technical basis for meeting risk-based remedial goals without pump-and-treat or excavation for sites where MNA is not viable. Develop/test engineered methods for maximizing attenuation of ⁹⁹ Tc in the subsurface. Concepts developed in scientific literature need to be tested under realistic environmental conditions and the most promising need to be further

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				developed and field tested. These will be applicable to current plumes and as contingencies for waste disposal facilities.
		Decommissioning and Disposal	Develop mitigation techniques for disposing ⁹⁹ Tc-contaminated equipment (fixants, packaging, barriers) (New)	Develop mitigation technologies, such as specialized packaging, barriers, and fixatives, to immobilize ⁹⁹ Tc on solid secondary wastes. This will result in technologies applicable to a range of solid secondary wastes, enabling options for disposal.
			Develop methods for removal of ⁹⁹ Tc from processing equipment (e.g., ingots, cascades) (New)	Develop methods to decontaminate processing equipment to enable disposal of ⁹⁹ Tc -contaminated materials (includes developing disposal options for secondary waste generated from decontamination).
Disposition	Behavior in the Environment	Controlling Processes	Evaluate IDF performance across a range of inventory assumptions (New) (1)	Evaluate the range of ⁹⁹ Tc inventories to determine performance-based limit. The current IDF PA is based on the assumption of very low ⁹⁹ Tc inventory. The results will aid in selecting disposal options for solid secondary wastes from WTP and elsewhere.
			Long-term radiological lysimeter program (SRR)	Measure the reduction capacity of radioactive samples by placing cementitious materials (saltstone or grout) and soils spiked with a suite of radionuclides or analogues in lysimeters. Results include K _d values in soil and cementitious materials, colloidal transport

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				measurements, and information about long-term geochemical and transport phenomena to support the waste release and transport models used in the Saltstone Disposal Facility (SDF), F-Area Tank Farm (FTF), and H-Area Tank Farm (HTF) performance assessments.
			Verify Tc mass balance to ensure that IDF meets acceptance criteria including distribution of ⁹⁹ Tc in WTP secondary wastes (New) (1)	Provide a technical basis for efficiency and utilization of WTP melter and off-gas equipment, along with improved prediction of ⁹⁹ Tc volatility to better project the quantity of ⁹⁹ Tc in WTP secondary wastes. Technetium- ⁹⁹ vaporizes in the LAW melter and is scrubbed by off-gas equipment. This task will evaluate the efficiency and utilization of the scrubber equipment to determine if remediation of ⁹⁹ Tc on secondary wastes will be necessary.
			Integrate fundamental understanding to quantify processes controlling subsurface contaminant fate and transport (New)	Integrate fundamental understanding of ⁹⁹ Tc distribution in the environment, chemical speciation, thermodynamics, and biogeochemistry into conceptual and numerical models. This effort will identify and quantify processes controlling ⁹⁹ Tc fate and transport into conceptual models and predictive simulations to determine behavior in the environment for final remediation and disposition of subsurface contamination.
		Predictive	Provide	Provide a framework for

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		Under-standing	predictive understanding to demonstrate engineered barriers will be effective in the long term (1000 years) (RL)	successful barrier implementation for groundwater protection. Long-term surface barriers are a candidate remedy for the deep vadose zone to reduce contaminant flux to groundwater. Data for a surface barrier at the Hanford Site has been assembled. A framework and predictive capability are needed for effective barrier implementation.
			Develop predictive tools to provide the technical basis for transitioning waste sites from active to passive remediation (New)	Quantify ⁹⁹ Tc distribution in the environment, chemical speciation, thermodynamics, and biogeochemistry to predict subsurface contaminant fate and transport and provide technical support for remediation and transitioning waste sites from active to passive remediation
	Risk Based Remediation	Source Term Behavior	Quantify retention/release mechanisms of ⁹⁹ Tc from in situ remediation processes (New)	Quantify release of ⁹⁹ Tc over time from vadose zone and groundwater by evaluating system response to amendments for in situ remediation. This effort will identify and quantify long-term behavior of in-situ remediation systems through experiments and predictive simulation to determine redox states and speciation.
	Endpoints	Fate in the Environment	Define risk-informed remediation end points (HQ)	Provide technical support for implementing risk-informed remediation endpoints based on predictive understanding of controlling processes and fate in the environment. Technical

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				<p>data predictions are needed to support risk-informed remediation endpoints (including MNA) for ⁹⁹Tc, consistent with existing guidance.</p>
			<p>Develop a better, and consistent (DOE, U.S. Nuclear Regulatory Commission [NRC], EPA) technical basis for concentration factors, dose conversion factors, and risk to human health (New)</p>	<p>Provide a technical basis for risk assessment parameters, including concentration and dose conversion factors for risk to human health. This effort will provide technical information that can be used to gain consistency in risk-assessment parameters across multiple agencies, including DOE, NRC, and EPA.</p>
	Monitoring	Technical Assistance	Develop and implement systems-based monitoring (HQ)	<p>Implement streamlined and cost-effective monitoring for remedy performance and long-term assessment. Methods are needed to process and make available monitoring data in real time, evaluate lines of evidence for remedy performance, and integrate the use of indicator parameters and diagnostic monitoring (e.g., mass flux).</p>
		Performance Verification	Develop innovative approaches for monitoring of vadose zone and groundwater contamination to verify	<p>Provide streamlined and cost-effective monitoring systems for the vadose zone. Methods need to be developed for measuring and controlling flux of contaminants in the vadose zone to support natural attenuation as well as monitoring systems that can</p>

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			remediation and natural attenuation (New)	provide real-time feedback during remedy implementation and performance.
			Integrate monitoring approaches with modeling for real-time assessment of remediation performance (HQ)	Provide a technical approach to assess current and future deep vadose zone contaminant distributions and flux to groundwater using integration of geophysical monitoring and simulations. Laboratory experiments are needed to reduce uncertainty in geophysical response, building on previous efforts.

Program Element	Focus Area	Activity	Tasks	FY13	FY14	FY15	FY16	FY17	FY18	FY19	FY20		
Characterization	Speciation and Chemistry	Redox Chemistry	⁹⁹ Tc Redox Speciation in (LAW) (HQ) (3)						ORP				
		Thermodynamics and Kinetics	Quantify effect of co-mingled contaminants on ⁹⁹ Tc behavior, transport and fate (RL)						RL				
			Define and quantify variables affecting biogeochemical controls on ⁹⁹ Tc behavior in soil and groundwater plumes (RL)						RL	PODP			
	Measurement Techniques	Non-pertechnetate	Develop methods to quantify and determine the speciation of ⁹⁹ Tc compounds in tank waste (WRPS) (3, complete)				ORP						
			Quantification and Identification of non-pertechnetate in tank waste samples (HQ) (3)					ORP					
			Non-Pertechnetate Sensor Development (HQ) (3)							ORP			
	In Situ/Real-Time Process Measurement	Real-time/in situ characterization and monitoring for geochemical and microbial properties and reactions (New)								RL			
	Inventory of Source Terms	Facilities	Characterize ⁹⁹ Tc in and cascades (New)							PODP			
		Waste Streams	Quantify inventory and behavior of ⁹⁹ Tc in solid secondary waste streams and residuals – in particular high-efficiency particulate air filters and submerged bed scrubber/wet electrostatic precipitator equipment (New) (3)									ORP	
		Groundwater and Soil	Quantify waste sources for subsurface contaminants through chemical fingerprinting and data mining (New)								ORP	RL	
Treatment	Separation	⁹⁹ Tc removal from LAW Recycle with Kurion media (WRPS) (2, complete)					ORP						
		Maturation of ⁹⁹ Tc ion exchange (Superlig® 639) (WRPS) (3)					ORP						
		Evaluation of Non-Ion Exchange Methods for ⁹⁹ Tc Removal (New) (3)									ORP		
		Treatment and removal of non-pertechnetate species from LAW (HQ) (3)										ORP	
		⁹⁹ Tc removal from LAW Off-Gas recycle stream (HQ) (2)					ORP						
		Evaluate long-term operational stability of resins used in ⁹⁹ Tc removal from aqueous streams (New)								RL			
	Immobilization	Understand, control, and improve ⁹⁹ Tc retention in glass processing (LAW and high-level waste [HLW]) (ORP)									ORP	SRS	
		Flowsheet modeling improvements for LAW recycle predictions (HQ) (2)					ORP						
		Develop non-glass waste forms specifically for technetium immobilization (HQ) (1)										ORP	SRS
		Zirconium Metal Organic Frameworks for Pertechnetate Removal (HQ, International Program)									ORP		
		Immobilization of Effluent Treatment Facility (ETF) secondary waste (WRPS)								ORP	SRS		
		Measure properties of laboratory-prepared Saltstone samples versus actual emplaced core samples and in-line process samples (Savannah River Remediation [SRR])						SRS					
		Technetium leaching characteristics from Saltstone monolith (SRR)						SRS					

Funding Source: DOE EM Headquarters (orange), DOE EM Site (yellow), Future Opportunity (green), Delivery to: ORP (red), RL (purple), SRS (orange), Paducah (blue)

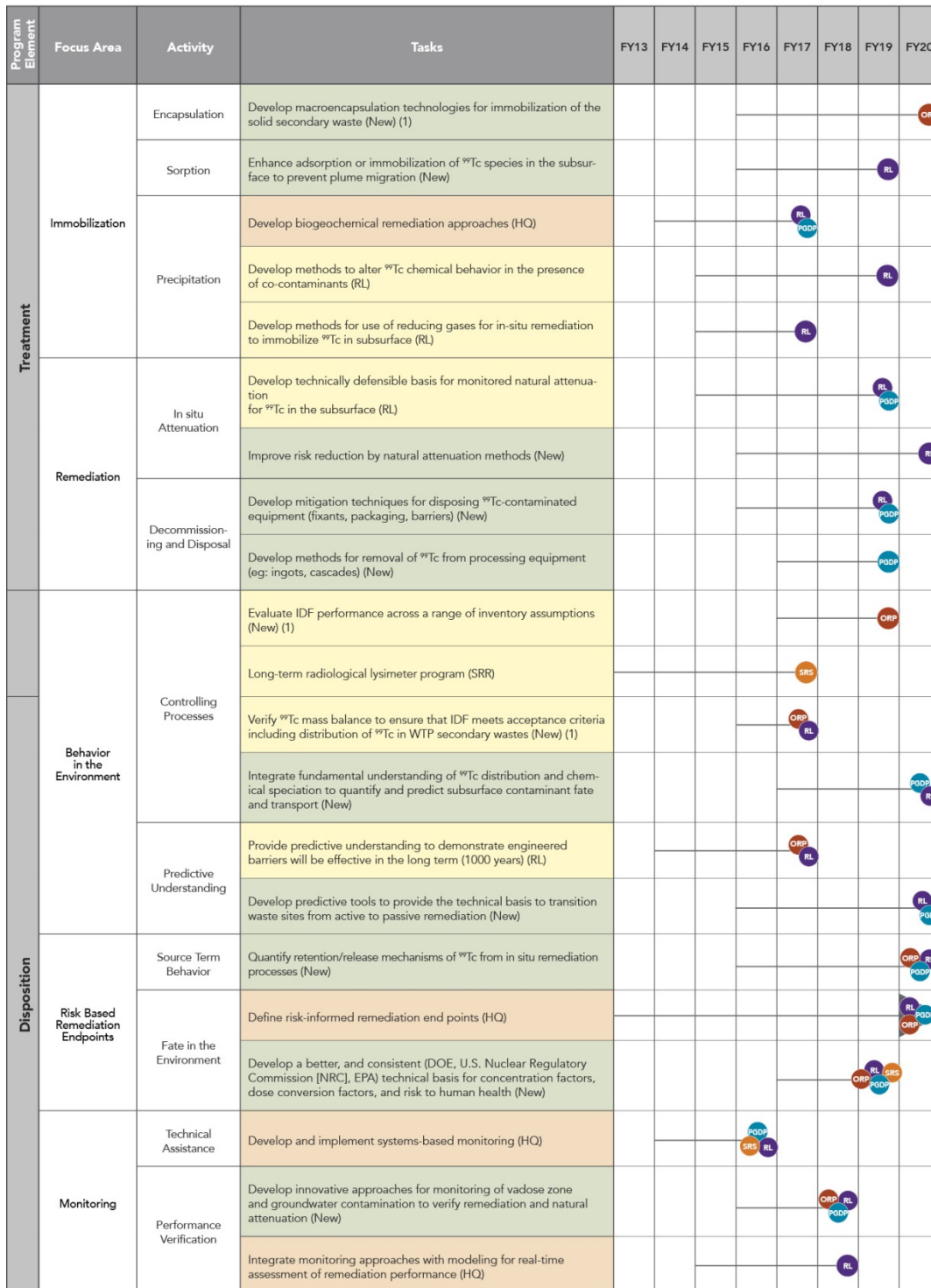


Fig. 1. Schedule and Logic for Technetium Management Tasks

CONCLUSIONS

This plan captures the principal technetium-related DOE EM needs and the approach that will be used to resolve them. This plan will be used as a framework for integrating and managing technical, budget, and schedule challenges associated with ^{99}Tc in waste tanks, facilities, and the environment. The plan provides a framework for reviewing results from projects, challenging what is learned, and developing specific scope that integrates with work being done by DOE site offices and contractors. The program will be implemented by field sites and HQ program offices acting in coordination, depending on funding, priority, and deployment timelines.

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